Supplementary Information

Rapid growth of fully-inorganic flexible Ca_xCoO_2 thin films from ligand free aqueous precursor ink for thermoelectric applications

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Formulation of DMF-complexes with Ca^{2+} and Co^{2+}

The hydrated acetate salts of Ca^{2+} ($Ca(CH_3COO)_2.H_2O$) and Co^{2+} ($Co(CH_3COO)_2.H_2O$) were taken as the precursor materials which were easily soluble in DMF. The DMF complexes of the metal ions namely, Ca^{2+}-DMF and Co^{2+}-DMF were prepared simply by adding the salts separately in a molar ratio 3:4 into the excess DMF, followed by stirring for 30 min at 60°C. After cooling at room temperature white precipitate of Ca^{2+}-DMF and violet precipitate of Co^{2+}-DMF appeared (as shown in Figure 1 (a)), which were re-precipitated (for 4-times) from hot DMF. Here, the precursor salts and DMF were procured from Sigma Aldrich.

Formulation of precursor thermoelectric ink

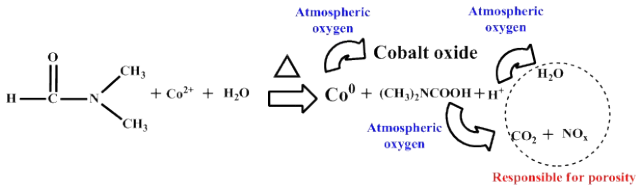
The precipitates were mixed together by dissolving in excess of DMF followed by stirring for 1 hour at 90°C. After cooling at room temperature, a purple color precipitate was obtained (as shown in Figure 1) which was re-precipitated from hot DMF (for 4-times) to remove the unwanted impurities. After washing with ether, the precipitate was dried at 60 °C to obtain a pink brown color precursor solid (as shown in extreme left of Figure 1(b)), which was easily soluble in de-ionized (DI) water to obtain a stable homogenous solution of bluish precursor ink having solid content of 10mg/mL.

Fabrication of thermoelectric samples

For the investigation thin films of $Ca_{0.35}CoO_2$ were grown by CSD method on sapphire and mica substrates. The ink was simply drop-casted onto the top-surfaces of cleaned substrates and heated to 700°C for 10 min in ambient condition. Subsequently, black-colored thin film of $Ca_{0.35}CoO_2$ appeared on the substrates. The plausible reaction mechanism is shown in Scheme S1.

Characterization

The crystal structure and morphology of the films were characterized by θ –2θ XRD analyses using monochromatic Cu Kα radiation (λ = 1.5406 Å) and scanning electron microscopy (SEM, LEO 1550 Gemini). The θ–2θ XRD scans were performed with a Philips PW 1820 diffractometer. Compositional analyses of the films were performed by energy dispersive X-ray spectroscopy (EDS) with an accuracy of ±5%. In-plane electrical resistivity and Seebeck coefficient were simultaneously measured as a function of temperature using an ULVAC-RIKO ZEM3 system.



Scheme S1. Reduction of Co^{2+} by DMF and formation of nanoporous $Ca_{0.35}CoO_2$ thin films.